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(54) **CLEANING AGENT FOR REMOVING POLYMER DEPOSITS FROM CONTAINERS**

(57) Polymer deposits, particularly those of vinyl chloride-containing copolymers, can be readily removed from polymerization containers by the use of a cleaning agent consisting of 100 parts by weight of water, 0-150 parts by weight of water-soluble organic solvents, 10-200 parts by weight of nonuniformly water-miscible organic solvents, 0-20 parts by weight of emulsifiers and 5-30 parts by weight of an alkali metal hydroxide and/or alkaline earth metal hydroxide.

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PATENT CLAIMS:

1. Cleaning agent for removing polymer deposits from containers, consisting of

   100 parts by weight (pbw) of water,
   0-150 pbw of water-soluble organic solvents,
   10-200 pbw of nonuniformly water-miscible organic solvents,
   0-20 pbw of emulsifiers, and
   5-30 pbw of an alkali metal hydroxide and/or alkaline earth metal hydroxide.

2. Cleaning agent according to Claim 1, characterized in that it contains per 100 parts by weight of water

   0-50 pbw of water-soluble organic solvents,
   30-100 pbw of nonuniformly water-miscible organic solvents,
   0.5-5 pbw of emulsifiers, and
   15-30 pbw of an alkali metal hydroxide and/or alkaline earth metal hydroxide.

3. Use of the cleaning agent according to one of the preceding claims for removing from polymerization reactors wall deposits of vinyl chloride copolymers, ethylenically unsaturated esters and optionally other comonomers, as well as wall deposits of SBR and/or SAN polymers.

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CLEANING AGENT FOR REMOVING POLYMER DEPOSITS FROM CONTAINERS

In the production and handling of aqueous polymer dispersions, including those obtained by the suspension, emulsion or microsuspension process, the formation of deposits on the container walls usually presents difficulties. Particularly critical is the formation of these deposits in polymerization reactors, because they can have an adverse affect on heat transfer and thus on the safety of the reactor operation as well as on product quality.

Hence, a multitude of processes and means for removing such wall deposits have already been proposed. In particular, unusual difficulties are encountered in the removal of wall deposits of copolymers made from vinyl chloride, ethylenically unsaturated esters and/or other comonomers, for example ethylene, especially after the emulsion polymerization process, and/or of deposits of crosslinked polymers.

Wall deposits of polymers from ethylenically unsaturated esters, particularly vinyl esters, have until now been dissolved by saponification with alcoholic solutions of alkali metal hydroxides and flushed out with water, which often causes the products of hydrolysis to reprecipitate. In many cases, it is therefore necessary to apply several flushing steps in sequence. When the copolymers also contain units of vinyl chloride (VC), the difficulties are even greater, because with increasing VC content, saponification resistance increases and the solubility of the saponification products is reduced.

If, for this reason instead of aqueous-alcoholic solvents purely organic solvent systems are used

(see, for example, US-A-34 75 218) in which, for example, polyvinyl chloride is soluble, then, in addition to occupational and environmental health problems as well as operational safety problems (fire hazard), new difficulties arise, because the polymer solutions reach high viscosities even at low solids contents and become difficult to handle and process.

Hence, the object of the present invention is to provide a cleaning agent which to a high degree avoids, and preferably altogether eliminates, the above-said difficulties of the prior art.
The cleaning agent should detach and take up polymer wall deposits without causing the liquid, despite high solids contents, to become highly viscous or even to lose its flowability altogether. Moreover, the discharged liquid should be readily worked up.

In particular, the cleaning agent should also make it possible to remove from containers residues or wall deposits of copolymers of vinyl chloride and ethylenically unsaturated esters. Particularly noteworthy in this regard are the wall deposits formed in the polymerization reactor during polymerization.

These objectives are reached in surprisingly advantageous manner by use of a cleaning agent which contains

100 pbw of water,
0 to 150, preferably 0-50 pbw of water-soluble organic solvents,
10 to 200, preferably 30-100 pbw of nonuniformly water-miscible organic solvents,
0-20, preferably 0.5-5 pbw of emulsifiers, and
5 to 30, preferably 15-30 pbw of an alkali metal hydroxide and/or alkaline earth metal hydroxide.

Preferred are organic solvents which are liquid at room temperature and have a boiling point from 50 and 170 °C, preferably from 50 to 150 °C. The water-soluble and the nonuniformly water-miscible solvents can be used individually or as mixtures.

Preferred water-soluble organic solvents are alcohols, ketones, dialkyl sulfoxides and/or ethers.

Particularly preferred are C_1 to C_3 alkanols, particularly methanol, ethanol, isopropanol and n-propanol; C_3 to C_5 ketones, particularly acetone and methyl ethyl ketone; water-soluble ethers, for example 1,4-dioxane, and dimethyl sulfoxide.

Preferred examples of nonuniformly water-miscible organic solvents are ethers, halogenated nonacidic hydrocarbons, aromatics and liquid, optionally halogenated paraffinic hydrocarbons. Particularly preferred are ethers, such as those that are liquid at room temperature, namely the dialkyl and/or alkyl benzyl ethers with C_1 to about C_6 alkyl groups, provided their boiling point at atmospheric pressure is in the indicated boiling range, for example those with CH_3-, C_2H_5-, C_3H_7-, C_4H_9-, C_5H_{11}- and C_6H_{13} alkyl groups, as well as dibenzyl ether, and particularly tetrahydrofuran (THF), and halogenated hydrocarbons which are also liquid at room temperature and boil in the indicated range, but do not possess acidic hydrogen atoms. Noteworthy are, in particular, carbon tetrachloride and especially perchloroethylene. Also preferred are aromatics, such as benzene, toluene and xylene, as well as paraffinic hydrocarbons.

Essential for the selection of the nonuniformly water-miscible solvents is their ability to dissolve, partly dissolve or at least swell organic polymers,

Emulsifiers are optionally added to the cleaning agent of the invention. This is preferred whenever the polymers to be detached from the container walls were prepared in the presence of only a small amount of emulsifier or no emulsifier at all, or the emulsifier was rendered ineffective in the course of the chemical reaction. The necessity to add an emulsifier can readily be determined in a few preliminary tests. The cleaning agent should be readily emulsifiable before use or during use. Commercial emulsifiers, preferably alkylsulfonates and/or alkylbenzenesulfonates, can be used.

Moreover, the cleaning agent of the invention contains an alkali metal hydroxide and/or alkaline earth metal hydroxide, preferably a hydroxide of lithium, sodium, potassium, cesium, rubidium, calcium, strontium and/or barium. Particularly preferred are calcium hydroxide and particularly sodium hydroxide and/or potassium hydroxide.

In the selection of the components which according to the invention are contained in the cleaning agent, it is important to make sure that said components will preferably not react with each other,

for example so as to convert the emulsifiers into water-insoluble calcium soaps, or the hydroxides, by reaction with the halogenated hydrocarbons, into alkali metal and/or alkaline earth metal halides. Hence, the organic solvents should not undergo appreciable hydrolysis at least while they are in use (for at the most 2 hours).

Particularly advantageous, especially for removing wall deposits of copolymers of vinyl chloride with comonomers such as ethylene, vinyl esters and/or (meth)acrylate esters, particularly with ethylene, vinyl acetate and/or C_1 to C_6 alkyl (meth)acrylates, and especially with those having high vinyl chloride contents, was found to be a mixture of water, acetone, perchloroethylene and sodium hydroxide and/or potassium hydroxide as well as, optionally, commercial sodium alkylsulfonates and/or particularly sodium alkylbenzenesulfonate, in which case the densities of the organic and aqueous phases are approximately equal. To achieve optimum results, the density of the lighter phase should, if possible, not differ from that of the heavier phase by more than, for example, 10%.

Surprisingly, even stubborn copolymer deposits dissolve leaving hardly any residue even after a short treatment period of, for example, 30 min to, for example, 2 hours, possibly with heating to about 100 °C. The resulting emulsions of the removed wall deposits are characterized by the fact that they can have a high solids content of, for example, 30 wt.%, based on the total weight, and that they can be removed from the container without problems, in most cases without leaving a residue, for example by slight rinsing with water or a small amount (particularly 5-20%, based on the reactor volume) of, for example, an alcohol indicated in the foregoing, optionally with brief heating. The work-up of the agents used can also be accomplished without any problems.

It is also surprising that, according to the invention, other difficultly soluble polymers, even partly crosslinked ones, can be removed without difficulty. Examples are the SBR and SAN polymers and mixture containing PVC. These wall deposits can also be readily removed with the afore-said mixture of acetone, perchloroethylene and sodium hydroxide and optionally an emulsifier.

As already mentioned, the work-up of the discharged cleaning emulsion containing the removed materials is very simple. Preferably, the mixture is first subjected to fractional distillation at atmospheric pressure. The residue is then preferably further purified by steam distillation until

the solvent content is below a desired limit. For example, the perchloroethylene content should be reduced to below 100 ppm and particularly below 30 ppm. The distillates can be worked up in the usual manner and the solvents reused. The still bottoms, which in most cases are liquid, contain essentially only a mixture of hydroxide, the optional emulsifier, and the polymer residues and water. For example, such still bottoms can be used with particular advantage to neutralize acidic residues in (even biological) waste liquid disposal. In addition, the polymer residues have the advantageous property of flocculating and thus can act as flocculating aids and in many cases also as precipitants for heavy metals which in this manner can be removed from the wastewater.

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PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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In re Application of:
Spencer Wayne Bruce et al

Serial No. 09/641,155 : Group Art Unit: 1746

Filed: August 17, 2000 : Examiner: not yet assigned

For: **Process For Cleaning Reactors**

Assistant Commissioner for Patents
Washington, DC 20231

CERTIFICATE OF MAILING

Sir:

I hereby certify that the following correspondence is being deposited with the U.S. Postal Service as first class mail in an envelope addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231 on the date indicated next to my signature below:

Supplemental Information Disclosure Statement
List of Art Cited by Applicant (in duplicate)
Copies of Cited Art
Postcard

January 23, 2001
Date

Shelley Daley
Signature